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A Comparative Review of Mathematical Models

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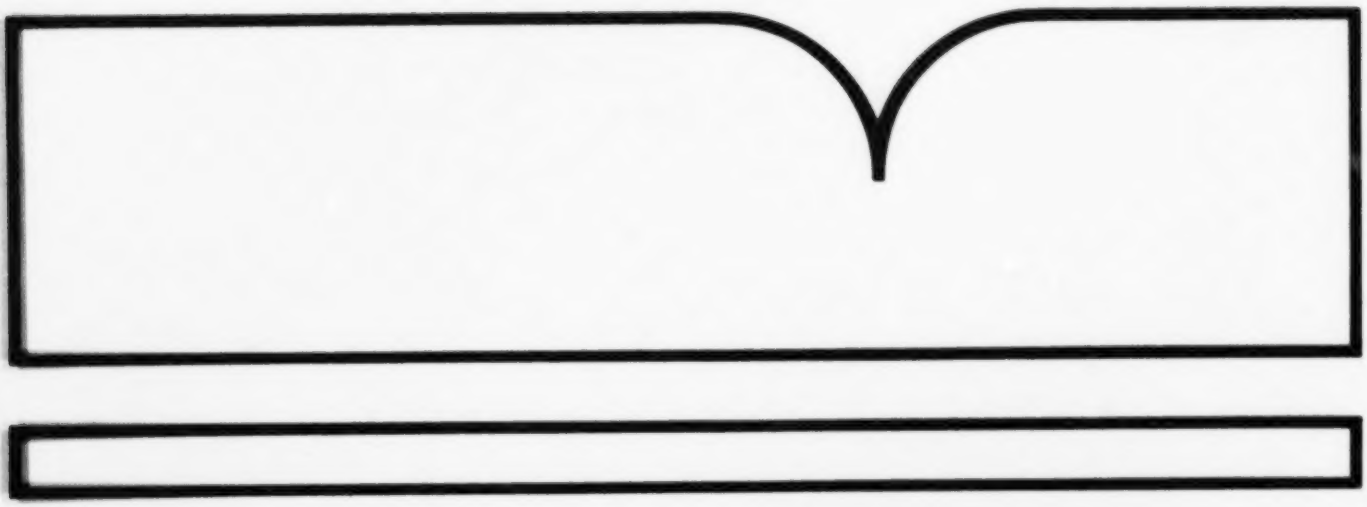

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16. ABSTRACT

Three modeling approaches are used that are based continuous, discrete (sectional), and parameterized representations of the aerosol size distribution. Simulations of coagulation and condensation are performed with the three models for clear, hazy and urban atmospheric conditions. Relative accuracies and computational costs are compared. Reference for the comparison is the continuous approach.

The results of the study provide useful information for the selection of an aerosol model, depending on the accuracy requirements and computational constraints associated with a specific application.

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JOURNAL ARTICLE

Simulation of Aerosol Dynamics: A Comparative Review of Mathematical Models

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A comparative review of mathematical models of aerosol dynamics is presented. Three approaches are considered that are based on continuous, discrete (sectional), and parametrized (lognormal) representations of the aerosol size distribution. Simulations of coagulation and diffusion-limited condensation are performed with these modeling approaches for three case studies typical of clear, hazy, and urban atmospheric aerosol concentrations. The relative accuracies and computational costs of models based on these approaches are compared. The models based on a continuous size distribution provide an accurate solution for both coagulation and condensation. Sectional approaches simulate coagulation very well but require a fine size resolution to minimize numerical diffusion in the simulation of condensation. The parametrized model based on log-normal modal size distributions is computationally efficient but tends to overestimate the rate of coagulation and the peak aerosol concentration resulting from condensational growth. The results of this study provide useful information for the selection of an aerosol model, depending on the accuracy requirements and computational constraints associated with a specific application.

INTRODUCTION

The study of aerosol system behavior is relevant to a variety of fields such as air pollution, combustion, and chemical engineering science. To understand the behavior of aerosol systems, it is necessary to be able to simulate by means of mathematical models the dynamic behavior of the aerosol population. Such simulations allow us to reconcile the theoretical description of the physical principles that govern aerosol systems with the experimental observation of these systems. Discrepancies between theory and experiment can then be analyzed and utilized to suggest theoretical advances and further experiments in the study of aerosol dynamics. To that end, several mathematical models have been developed to simulate the physical processes that affect aerosols. Such processes include coagulation, growth due to

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condensation of gases, shrinkage due to evaporation, nucleation of new aerosols, sedimentation, and deposition on surfaces.

We focus in this work on the simulation of coagulation and condensation in aerosol systems because most difficulties in solving the equations representing aerosol system dynamics concern the coagulation and condensation terms. The objective of this work is to compare the accuracy and computational requirements of several approaches to simulating aerosol dynamics.

We compare three major approaches that have been developed to simulate aerosol dynamics. These three types of mathematical models are applied to various test cases, and the simulation results and computational requirements are quantitatively compared. The three major approaches differ primarily by their representation of the size distribution of aerosols:

1. Continuous representation
2. Discrete representation
3. Parametrized representation

Each of these approaches is a numerical technique for solving the general dynamic equation for aerosols. They differ only in their degree of approximation of the size distribution. Those techniques that offer any desired degree of approximation are referred to as continuous. Discrete approximations are methods in which the size domain is divided into discrete segments or sections. In principle, discrete approaches can be implemented at an arbitrary degree of approximation; however, there are practical constraints on the number of sections that can be used. Finally, parametrized representations are those methods in which the size distribution is assumed to adhere to a known form depending on a small number of parameters. Both continuous and discrete approaches necessarily assume a certain form of the size distribution but generally at a much finer level of representation than do the approaches that we classify as parametrized.

We present in the next section the basic equations that govern the evolution of a particulate system undergoing coagulation and condensation. The following section describes the modeling techniques that are evaluated in this comparative study. We then describe the simulations for the selected case studies and discuss the resulting accuracy and computational costs for coagulation and condensation, respectively. Concluding remarks and recommendations are provided in the last section.

THE GENERAL DYNAMIC EQUATIONS GOVERNING AEROSOL SYSTEMS

We present in this section the basic equations that govern the dynamics of spatially homogeneous particulate systems undergoing coagulation and condensation. Let $n(v, t)$ be the density function of the aerosol number size distribution, where v is the aerosol volume and t is the time, i.e., $n(v, t)\,dv$ is the number of aerosols per unit volume of air, with volumes between v and $v + dv$.

The evolution of the aerosol size distribution due to coagulation is represented by the following integrodifferential equation:

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_{v^*}^{v} \beta(v-\tilde{v},\tilde{v})\,n(\tilde{v},t) \times n(v-\tilde{v},t)\,d\tilde{v} - \int_{0}^{\infty} \beta(v,\tilde{v})\,n(v,t)\,n(\tilde{v},t)\,d\tilde{v},$$

$$n(v,0) = n_0(v), \qquad (1)$$

$$n(v,t) = 0, \qquad v < v^*,$$

where β is the coagulation coefficient and v^* is the minimum aerosol volume. Difficulties in solving this equation arise in the evaluation of the integrals on the right-hand side.

The coagulation coefficient β is a function of the size of the two coagulating aerosols. Its form depends on the coagulation process, i.e., Brownian, turbulent, or gravitational

motion. For the purpose of this study, we consider coagulation by Brownian motion since it is the most relevant to coagulation of atmospheric fine aerosols (e.g., Seigneur and Barnes, 1985). The aerosol coagulation coefficient used in this study is the Fuchs coefficient (Fuchs, 1964; Sitarski and Seinfeld, 1977):

$$\beta(v_i, v_j) = 4\pi(D_i + D_j)(r_i + r_j) \times \left[\frac{r_i + r_j}{r_i + r_j + g_{ij}} + \frac{4(D_i + D_j)}{(\bar{C}_i^2 + \bar{C}_j^2)^{1/2}(r_i + r_j)} \right]^{-1} \quad (2)$$

where r_i is the radius of aerosols of volume v_i, d_i is the diffusion coefficient of aerosols of volume v_i, g_{ij} is a function of the aerosol radius and mean free path of the air, and $\bar{C}_i$ is the mean thermal velocity of aerosols of volume v_i.

The evolution of the aerosol size distribution due to condensation/evaporation is represented by the following equation:

$$\frac{\partial n(v,t)}{\partial t} = -\frac{\partial}{\partial v}[n(v,t)I(v,t)],$$
$$n(v,0) = n_0(v),$$
$$n(v,t) = 0, \qquad v < v^*, \quad (3)$$

where $I(v, t) = dv/dt$, the rate of growth/shrinkage of a particle of volume v.

Equation (3) is a hyperbolic partial differential equation. The numerical solution of such an equation is hindered by the difficulty in accurately representing the fronts that move with velocity dv/dt. The errors in the solution give rise to numerical diffusion and dispersion (Tsang and Brock, 1983). Numerical diffusion leads to a decrease of the peak values of the number distribution and to concurrent increases in the values of the number distribution around these peak values. Numerical dispersion leads to wakes in the ranges below and above the area of large values of the number distribution. If one is interested only in condensation/evaporation processes, then Eq. (3) can be solved exactly by the method of characteristics. However, in the presence of coagulation, the condensation/evaporation term of the general dynamic equation must be treated numerically in accordance with the coagulation terms.

In this study the condensation growth law, dv/dt, which depends on the condensing vapor and aerosol size, is represented by the Fuchs–Sutugin formula (Fuchs and Sutugin, 1971):

$$\frac{dv}{dt} = \frac{4\pi r D}{1 + \left(\frac{1.333\mathrm{Kn} + 0.71}{1 + \mathrm{Kn}}\right)\mathrm{Kn}} \times v_m \left[P - P_s \exp\left(\frac{2\sigma v_m}{rkT}\right) \right], \quad (4)$$

where r is the aerosol radius, D is the diffusion coefficient of the condensing vapor, Kn is the Knudsen number equal to λ/r, λ is the mean free path of the condensing vapor, v_m is the molecular volume of the condensing vapor, and P and P_s are the ambient and equilibrium vapor pressure of the condensing vapor, respectively. The exponential term represents the Kelvin effect, where σ is the surface tension of the condensed species, k is Boltzmann's constant, and T is the absolute temperature.

Species such as condensible organics generally have a nonnegligible equilibrium vapor pressure; thus the Kelvin effect becomes important and can lead to evaporation from small aerosols while condensation occurs on larger aerosols (Tsang and Brock, 1983, 1984). In this study, we focus on the treatment of condensation only and therefore assume that the equilibrium vapor pressure of the condensing vapor is zero. This is a reasonable assumption for a condensing species with very low volatility such as sulfuric acid.

DESCRIPTION OF THE MATHEMATICAL MODELS OF AEROSOL DYNAMICS

This section describes the mathematical models that were selected for our compara-

tive study of the continuous, discrete, and parametrized approaches to simulating aerosol dynamics. We consider the models of Brock and co-workers based on the continuous aerosol size distribution, the model of Seinfeld and co-workers based on a discrete representation of the aerosol size distribution, and the parametrized aerosol model of Whitby and co-workers.

Models Based on the Continuous Representation of the Aerosol Size Distribution

Suck and Brock (1979), Tsang and Brock (1982, 1983), and Yom and Brock (1984) have developed mathematical models to simulate the evolution of the aerosol number distribution, $n(v, t)$, when it is affected by either coagulation or condensation/evaporation. We briefly describe in this section the formulation of the models COAGUL and CONFEMM, which simulate coagulation and condensation, respectively.

The model COAGUL is based on the solution of the coagulation equation, Eq. (1). Suck and Brock (1979) then performed the following change of variable, the so-called J-space transformation:

$$v(J) = v(J_0)\exp[\alpha(J - J_0)], \tag{5}$$

where J and J_0 are integers such that $J \geq J_0$, $J_0 > 0$, and α is an adjustable parameter.

The aerosol distribution function in J space is then represented by the following function:

$$\psi(J, t) = \alpha v(J) n(v(J), t). \tag{6}$$

The coagulation equation may then be rewritten for the J-space distribution function as follows:

$$\frac{\partial \psi(J, t)}{\partial t} = \int_{J_0}^{J_h} \beta_J(\tilde{J}, J') \frac{v(J)}{v(\tilde{J})} \psi(\tilde{J}, t)\psi(J', t)\, dJ' - \int_{J_0}^{\infty} \beta_J(J, J')\psi(J, t)\psi(J', t)\, dJ', \tag{7}$$

where

$$\tilde{J} = J + \frac{1}{\alpha}\ln\{1 - \exp[\alpha(J - J')]\};$$

$$J_h = J - \frac{\ln 2}{\alpha};$$

and

$$\beta_J(\tilde{J}, J') = \beta(v - v', v').$$

The integrals in Eq. (7) are then represented by means of cubic spline functions, and a subroutine based on the method of Gear (1971) is used to integrate the resulting ordinary differential equations with respect to time. The solution $\psi(J, t)$ is then converted back to the number distribution function $n(v, t)$ according to Eq. (6).

The model CONFEMM is based on the solution of the condensation equation for the continuous number distribution, as described by Eq. (3). Tsang and Brock (1983) developed numerical schemes for solving this equation that minimize numerical diffusion and dispersion to any desired level of accuracy. They used two different finite-element methods for the condensation ($dv/dt > 0$) and evaporation ($dv/dt < 0$) equations. The method of Varoglu and Finn (1980) was modified and applied to the solution of the condensation equation. The method of Neuman (1981), together with cubic spline interpolation on finite elements, was applied to the solution of the evaporation equation. These two approaches yield solutions with any specified degree of accuracy. In addition, the two techniques have been coupled to solve the equation representing the case in which both condensation and evaporation simultaneously affect the aerosol size distribution (Tsang and Brock, 1984). In the present study, we consider the condensation equation only.

Model Based on the Discrete Representation of the Aerosol Size Distribution

In the discrete approach to modeling aerosol dynamics, the aerosol size range is divided into a discrete number of sections.

The aerosol volumes of section l range from v_{l-1} to v_l, where $l = 1, \ldots, L$. Approximating the number, surface area, or volume distribution function as a constant within each section results in a set of differential equations for the properties of each section. For example, the number distribution is approximated as follows:

$$N_l(t) = \int_{v_{l-1}}^{v_l} n(v,t)\,dv, \qquad l = 1, \ldots, L, \tag{8}$$

where $N_l(t)$ is the aerosol number concentration in section l, L is the total number of aerosol size sections, and v_0 and v_L are the aerosol volume of the lower and upper ranges of the aerosol size distribution, respectively.

The number distribution $n(v,t)$ is then approximated by the step functions $N_l(t)(v_l - v_{l-1})^{-1}$. The volume size distribution is approximated in a similar manner, as follows:

$$Q_l(t) = \int_{v_{l-1}}^{v_l} n(v,t)\,v\,dv, \qquad l = 1, \ldots, L. \tag{9}$$

The aerosol dynamic equations can be solved for any representation of the size distribution, i.e., number, volume, etc. Generally, the sectional equations are solved for the mass or volume distribution. This solution is convenient because it allows direct conservation of mass or volume. In addition, it is computationally more accurate because the volume distribution covers a lesser range of concentration values than does the number distribution.

The coagulation equation for the sectional volume distribution can be deduced from Eq. (1) to give the following ordinary differential equations (Gelbard, Tambour, and Seinfeld, 1980):

$$\frac{dQ_l(t)}{dt} = \int_{i=1}^{l-1} {}^a\bar{\beta}_{i,l-1} Q_i(t) Q_{l-1}(t) - \sum_{i=1}^{L} {}^b\bar{\beta}_{i,l} Q_i(t) Q_l(t), \qquad l = 1, \ldots, L, \tag{10}$$

where the first term is not evaluated for $l = 1$.

The first term represents the formation of new aerosols in section l by coagulation of aerosols from lower sections, and the second term represents the coagulation of aerosols from section l with other aerosols to form aerosols in higher sections.

The sectional coagulation coefficients ${}^a\bar{\beta}_{i,l-1}$ and ${}^b\beta_{i,l}$ are calculated by integrating the coagulation coefficient $\beta(v_1, v_2)$ given by Eq. (2) over the sections of interest (see Gelbard, Tambour, and Seinfeld, 1980, for the derivation of the sectional coagulation coefficients). These coefficients are generally calculated with the constraint that $v_l > 2v_{l-1}$. The advantage of this method is that for a fixed sectionalization of the aerosol size distribution, the sectional coagulation coefficients are integrated only once, and the coagulation equation is then reduced from an integrodifferential equation to a set of ordinary differential equations.

Similarly, the condensation equation governing the sectional volume distribution can be deduced from Eq. (3) to give the following equation (Gelbard and Seinfeld, 1980):

$$\frac{dQ_l(t)}{dt} = {}^a\bar{\phi}_l Q_l(t) + {}^b\bar{\phi}_{l-1} Q_{l-1}(t) - {}^b\bar{\phi}_l Q_l(t), \qquad l = 1, \ldots, L, \tag{11}$$

where the second term is not evaluated for $l = 1$. The first term represents the growth of the aerosol volume in section l due to condensation; the second term represents the growth of the aerosol volume from section $(l-1)$ into section l; and the third term represents the growth of the aerosol volume from section l into section $(l+1)$. The sectional condensation coefficients are calculated by integrating the growth law given by Eq. (4) over the sections (Gelbard and Seinfeld, 1980; Seigneur, 1982). If the sectionalization of the aerosol size distribution is fixed, these sectional condensation coefficients are calculated only once, and the condensation equation is then reduced from a

partial differential equation to a set of ordinary differential equations. In addition to including the treatment of condensation and evaporation processes in Eq. (11), Warren and Seinfeld (1985) improved the sectional treatment of gas/aerosol conversion by calculating coefficients that allow conservation of the aerosol number concentration. Their formulation was used in this study.

The model ESMAP (Warren and Seinfeld, 1985)—an extension of the model MAEROS (Gelbard and Seinfeld, 1980; Gelbard, 1984)—combines the treatment of both coagulation and condensation to describe the evolution of a sectional aerosol size distribution affected by these two processes. The sectional coagulation and condensation coefficients are calculated by Gaussian quadrature. The set of ordinary differential equations is solved by the numerical intergration scheme EPISODE, a revised version of the numerical integration scheme of Gear (Byrne and Hindmarsh, 1975).

Model Based on the Parametrized Representation of the Aerosol Size Distribution

Whitby (1981a) developed the model AGRO, which simulates the evolution of a bimodal aerosol size distribution. The model is based on the parametrization of the coagulation and condensation processes and describes the evolution of the number and volume concentrations of the two models. The fixed number of parameters involved in the model formulation does not allow for variation of the resolution of the aerosol size distribution as was possible in the models described above, and the parametrized approach is constrained by this definition of the two modes. These two modes represent fine aerosols (i.e., up to 3 μm in diameter) and consist of a nuclei mode and an accumulation mode. The coarse mode is assumed to be affected by emissions, sedimentation, and deposition processes but not by coagulation and condensation processes. It is therefore treated separately from the two fine aerosol modes. The bimodal number distribution for fine aerosols, $n(d, t)$, represents the aerosol number concentration as a function of $\log(d)$, where d is the aerosol diameter. This distribution is represented by two lognormal distributions as follows:

$$n(d,t) = \frac{N_n(t)}{(2\pi)^{1/2}\log[\sigma_n(t)]} \times \exp\left[-\frac{1}{2}\left(\frac{\log[d/d_{Nn}(t)]}{\log\sigma_n(t)}\right)^2\right] + \frac{N_a(t)}{(2\pi)^{1/2}\log[\sigma_a(t)]} \times \exp\left[-\frac{1}{2}\left(\frac{\log[d/d_{Na}(t)]}{\log\sigma_a(t)}\right)^2\right], \quad (12)$$

where the subscripts n and a refer to the nuclei and accumulation modes, respectively, N_n and N_a represent the total aerosol number concentrations in each mode, d_{Nn} and d_{Na} are the geometric mean aerosol diameters, and σ_n and σ_a are the standard deviations. Similarly, the bimodal volume distribution, $V(d, t)$, represents the aerosol volume concentration as a function of $\log(d)$. It is represented by the sum of two log-normal distributions as follows:

$$V(d,t) = \frac{V_n(t)}{(2\pi)^{1/2}\log[\sigma_n(t)]} \times \exp\left[-\frac{1}{2}\left(\frac{\log[d/d_{Vn}(t)]}{\log[\sigma_n(t)]}\right)^2\right] + \frac{V_a(t)}{(2\pi)^{1/2}\log[\sigma_a(t)]} \times \exp\left[-\frac{1}{2}\left(\frac{\log[d/d_{Va}(t)]}{\log[\sigma_a(t)]}\right)^2\right], \quad (13)$$

where V_n and V_a represent the total aerosol volumes in each mode, and d_{Vn} and d_{Va}

represent the geometric mean aerosol diameters. A third log-normal distribution with constant parameters was added in this study to represent the coarse mode.

In the original formulation (Whitby, 1981a), the coagulation equations consist of a set of four ordinary differential equations representing the temporal evolution of these four parameters, and four algebraic equations calculating the mean diameters; the standard deviations were kept constant:

$$\frac{dN_n(t)}{dt} = -K_{nn}N_n^2(t) - K_{na}N_n(t)N_a(t),$$

$$\frac{dN_a(t)}{dt} = K_{na}N_n(t)N_a(t) - K_{aa}N_a^2(t),$$

$$\frac{dV_n(t)}{dt} = -K_{na}N_a(t)N_n(t)\frac{\pi}{6}(d_{Nn})^3 \times \exp(4.5\ln^2\sigma_n), \quad (14)$$

$$\frac{dV_a(t)}{dt} = K_{na}N_a(t)N_n(t)\frac{\pi}{6}(d_{Nn})^3 \times \exp(4.5\ln^2\sigma_n).$$

The parameters K_{nn}, K_{aa}, and K_{na} are the nuclei intramodal, accumulation intramodal, and nuclei/accumulation intermodal coagulation coefficients, respectively. They are derived from the Fuchs coagulation coefficient given in Eq. (2) integrated over log-normal distibutions. These parameters depend therefore on the standard deviations and mean diameters of the modal distribution (Whitby, 1985). The first equation represents the decrease in aerosol number in the nuclei mode due to intramodal coagulation of nuclei mode aerosols and intermodal coagulation of nuclei mode aerosols with accumulation mode aerosols. The second equation represents the change in aerosol number in the accumulation mode due to intermodal coagulation of nuclei mode aerosols with accumulation mode aerosols and intramodal coagulation of accumulation mode aerosols. The change in volume concentrations results from intermodal coagulation only. This value is calculated from the intermodal coagulation term of the number concentrations and converted into volume concentrations.

In a new version of the model AGRO, both the mean diameters for the number and volume distributions and the standard deviations are allowed to change with time. Two additional equations are therefore introduced to calculate the temporal evolution of the standard deviations. The algorithms for calculating the evolution of these parameters are given by Whitby (1985).

The effect of condensation on the aerosol size distribution is treated similarly by a set of ordinary differential equations:

$$\frac{dV_n(t)}{dt} = Q_{Vn},$$

$$\frac{dV_a(t)}{dt} = Q_{Va}, \quad (15)$$

where Q_{Vn} and Q_{Va} are the rates of condensation of the nuclei and accumulation modes, respectively. These condensation rates depend on the rate of condensible species formation in the gas phase given by Eq. (4) and the distribution of condensation between the two modes. This distribution is determined according to the Fuchs–Sutugin condensation formula given in Eq. (4).

These differential equations representing coagulation and condensation are combined into the model AGRO. The numerical solution is obtained by a finite-difference technique with variable time steps.

SIMULATION OF AEROSOL COAGULATION AND CONDENSATION

The models AGRO, ESMAP, COAGUL, and CONFEMM were applied to the simulation of (1) coagulation, and (2) condensation for atmospheric aerosol concentrations typical of clear, hazy, and urban conditions. The aerosol size distributions were modeled for the 0.001–10-μm-diam size range. Two resolutions were used for ESMAP: 12 and 39 sections for this size range.

The simulations were conducted for 12 hr. The condensation rates were calculated with a gas-phase chemical kinetic mechanism for sulfuric acid formation. The sulfuric acid

TABLE 1. Initial Log-Normal Size Distributions Used in the Aerosol Dynamics Model Simulations

Parameter[a]	Conditions		
	Clear	Hazy	Urban
Mean diameter (μm)			
d_n	0.03	0.044	0.038
d_a	0.2	0.24	0.32
d_c	6.0	6.0	5.7
Standard deviation			
σ_n	1.8	1.2	1.8
σ_a	1.6	1.8	2.16
σ_c	2.2	2.2	2.21
Total volume ($\mu m^3 cm^{-3}$)			
V_n	0.03	0.09	0.63
V_a	1.0	5.8	38.4
V_c	5.0	25.9	30.8
Reference	Seigneur (1982)	Whitby (1981b)	Whitby (1978)

[a]Subscripts n, a, and c refer to nuclei, accumulation, and coarse modes, respectively.

formation rates amounted to 0.3, 5.5, and 4.6 $\mu m^3\ cm^{-3}$ of aerosol for 12 hr for typical clear, hazy, and urban conditions, respectively. The condensation rates were assumed to be constant throughout the simulation.

The initial size distributions were chosen to be log–normal to allow all three models to be initialized with identical size distributions. These initial size distributions are presented in Table 1. The models AGRO, COAGUL, and CONFEMM used the parameters of the log-normal size distributions as direct inputs. The log-normal size distributions were integrated exactly over 12 and 39 size sections to provide the inputs to ESMAP.

The aerosol size distributions were quantitatively compared after 12 hr of simulation as follows. The COAGUL and CONFEMM simulation results were taken as reference since they are capable of the most highly resolved solutions of the coagulation and condensation equations, respectively. Test simulations of COAGUL were made using 79, 39, and 13 grid points. The maximum local error between the simulations using 39 grid points and those using 79 grid points was 3% over the diameters of interest. The maximum error for the simulations using 13 grid points was 5%. The CONFEMM simulations used 80, 40, and 12 grid points. The maximum error between the 40- and 80-point simulations was 1.5%. The maximum error using 12 points was 16%. Computational costs increased significantly as the number of grid points increased. The increase in cost is nearly proportional to the number of grid points for CONFEMM and more than proportional for COAGUL. Since reasonable accuracy was obtained in the simulations using 39 and 40 points for COAGUL and CONFEMM, respectively, these model results were used as reference in this study.

Once satisfactory grid point numbers were selected, it was then necessary to allow a common representation of the size distributions. To that end, the COAGUL and CONFEMM results were cast into a sectional form with 12 and 39 size ranges. This sectionalization was carried out by interpolating between the points of the COAGUL and CONFEMM distributions by means of a cubic spline function and integrating the resulting size distributions over the desired size ranges. The results of the model ESMAP with 12 and 39 sections were compared with

the results of COAGUL and CONFEMM sectionalized with 12 and 39 size ranges, respectively. The size distributions calculated by AGRO were cast into a sectional size distribution by means of an exact analytical transformation. The AGRO results could then be compared with the COAGUL and CONFEMM results using the 39-section size resolution. The accuracy of this technique for comparing the size distributions calculated by the various models was assessed by applying it to the initial size distributions, which are necessarily identical for all models. This evaluation showed that the technique was accurate over the entire size range within 1% and locally within 2%.

A quantitative comparison of model accuracy was conducted for aerosols with diameters in the size range 0.07–2.5 μm. Below 0.07 μm, aerosol concentrations were very low after 12 hr of simulated coagulation or condensation, and comparison of predicted aerosol concentrations would therefore be of little value. Above 2.5 μm, aerosols are little affected by coagulation and condensation, and all calculated size distributions after 12 hr are nearly identical to the initial size distribution; thus, model comparison in the upper size range is irrelevant. It may be noted that the size range 0.07–2.5 μm comprises the aerosols that are optically the most active and generally includes the largest volume of secondary aerosols.

The model comparison was performed with the following measure:

$$D = \frac{1}{15} \sum_{i=19}^{33} \frac{|Q_i - Q_i^*|}{Q_i^*}, \qquad (16)$$

where i is the section number of the 39-section representation and corresponds to the size range 0.07–2.5 μm, Q_i^* is the aerosol volume in section i calculated by either COAGUL (coagulation simulations) or CONFEMM (condensation simulations), and Q_i is the aerosol volume in section i calculated by ESMAP (39 sections), ESMAP (12 sections), or AGRO. A model that provides the same result as the reference model will ideally have a performance measure of 0% (actually, the limitations of the interpolation method may lead to a value of D of 1%), whereas a model that differs widely from the reference model will have a large value of D.

Simulation of Coagulation

The results of the simulations of coagulation are presented for the volume size distribution in Figures 1–3 for clear, hazy, and urban conditions. The results of the model performance evaluation [Equation (16)] are presented in Table 2. In theory, total aerosol mass is conserved during coagulation. Total aerosol mass conservation was checked for COAGUL, ESMAP (both 12 and 39 sections), and AGRO. After 12 hr of simulation time, all models were found to conserve mass to within 0.5% for all three cases.

It appears that for clear conditions, where aerosol concentrations are very low, coagulation has little effect on the aerosol size distribution. Thus, after 12 hr of simulation, all models provide results that are very close to the initial size distribution, and the ESMAP and AGRO simulation results are within 1% and 2% of the COAGUL simulation results, respectively.

For hazy conditions, a similar result is obtained; aerosol concentrations are not high enough to allow coagulation to significantly affect the initial size distribution. It may be noted, however, that AGRO tends to predict a slightly larger peak in the accumulation mode than do COAGUL and ESMAP. The performance of ESMAP and AGRO is still excellent for this case.

The simulation of urban aerosol concentrations is a more stringent test for coagulation models since there is a significant change in the aerosol size distribution during the 12-hr simulation. The COAGUL simulation shows that aerosols below 0.15 μm coagulate with aerosols of larger sizes to lead to an increase in the peak concentration of the accumulation mode. The mean diameter of the coagulation mode is not noticeably

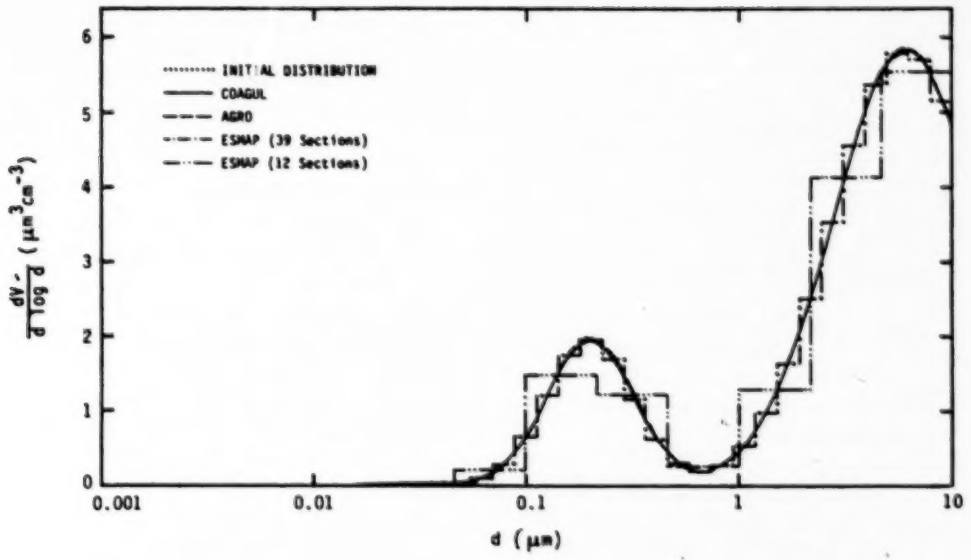
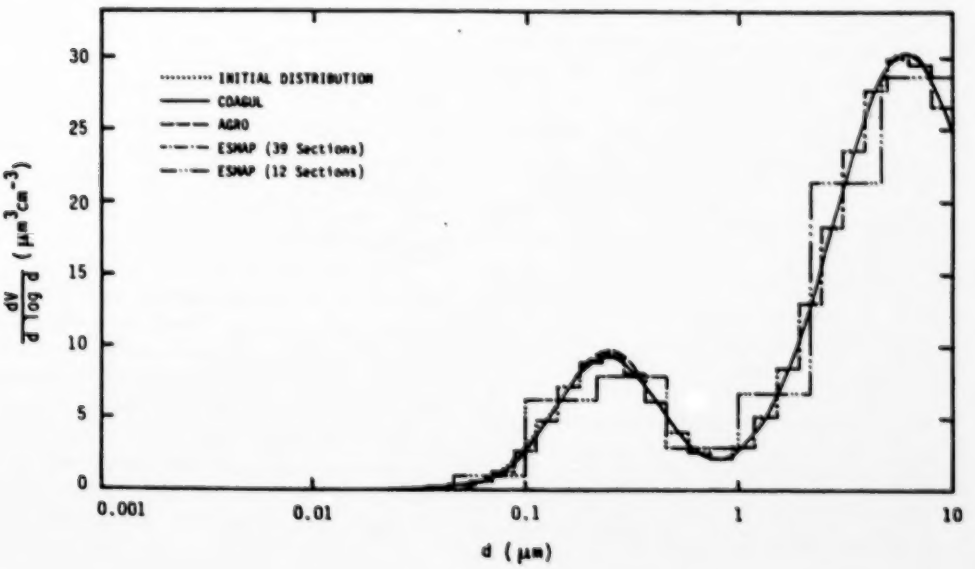


FIGURE 1. Simulation of coagulation for clear conditions; aerosol volume distributions, initially and after 12 hr.

FIGURE 2. Simulation of coagulation for hazy conditions; aerosol volume distributions, initially and after 12 hr.

affected by the coagulation process. The change in the aerosol size distribution is negligible above 0.7 μm. The ESMAP simulation results closely approximate those of COAGUL, producing size distributions that are within a few percent. The AGRO simulation tends to overestimate the rate of coagu-



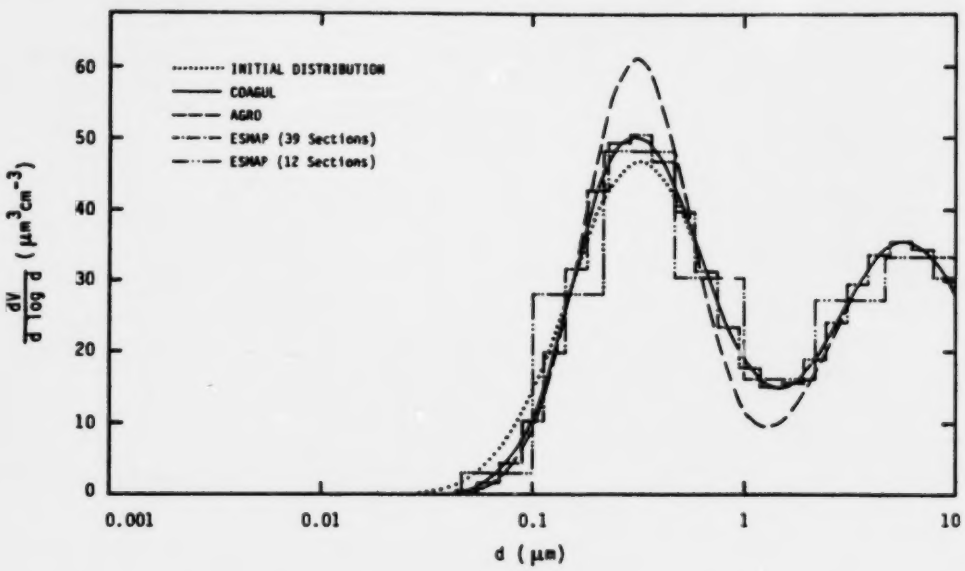


FIGURE 3. Simulation of coagulation for urban conditions; aerosol volume distributions, initially and after 12 hr.

lation and leads to results that are, on average, within 20% of the COAGUL simulation results. The mean diameter of the accumulation mode is well predicted by AGRO; however, the standard deviation is too small, resulting in overprediction of the aerosol concentration at the mean diameter size and underprediction at the tails of the accumulation mode distribution. This overprediction of the overall coagulation rate by AGRO is due to the inherent assumption of a log-normal distribution.

This discrepancy between the results of AGRO and COAGUL can be better exemplified by analyzing the evolution of the number distributions since the coagulation equation is based on the number concentrations. As shown in Figure 4, COAGUL does not predict a log-normal distribution for the aerosol number distribution, and there is a sharp cutoff in the number concentrations at the lower size end. In contrast, AGRO requires the assumption of a log-normal distribution and, therefore, the number distribution extends further toward the lower size range. The coagulation rate increases as the difference between the aerosol sizes increases. Therefore, the AGRO number size

TABLE 2. Comparison of Model Simulation Results for Coagulation

Model	Average absolute normalized difference (percent)		
	Clear conditions	Hazy conditions	Urban conditions
COAGUL		(Reference)	
ESMAP (39 sections)	1	1	2
ESMAP (12 sections)	1	1	3
AGRO	2	2	18

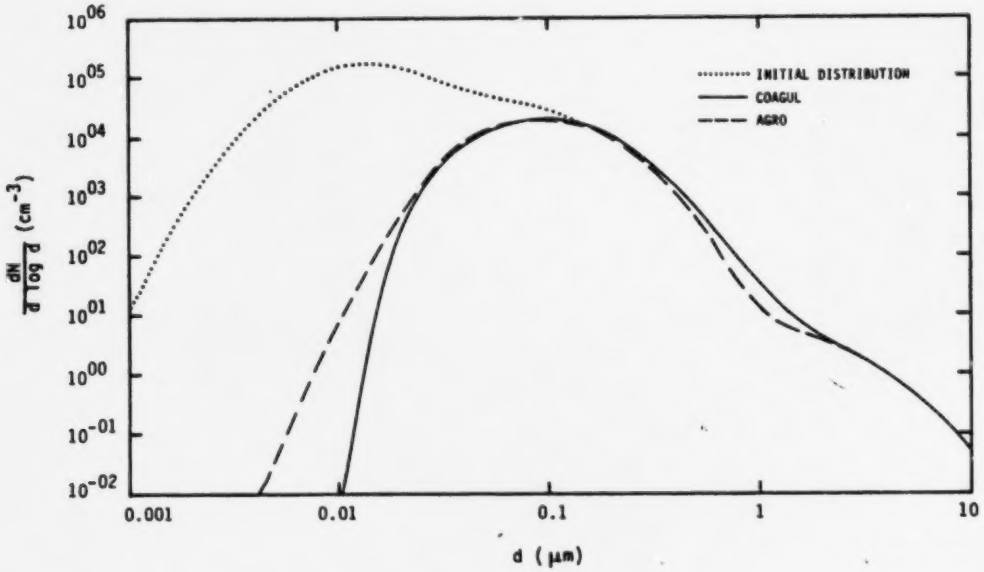


FIGURE 4. Simulation of coagulation for urban conditions; aerosol number distributions, initially and after 12 hr.

distribution allows coagulation to proceed at a faster rate than does the COAGUL number size distribution.

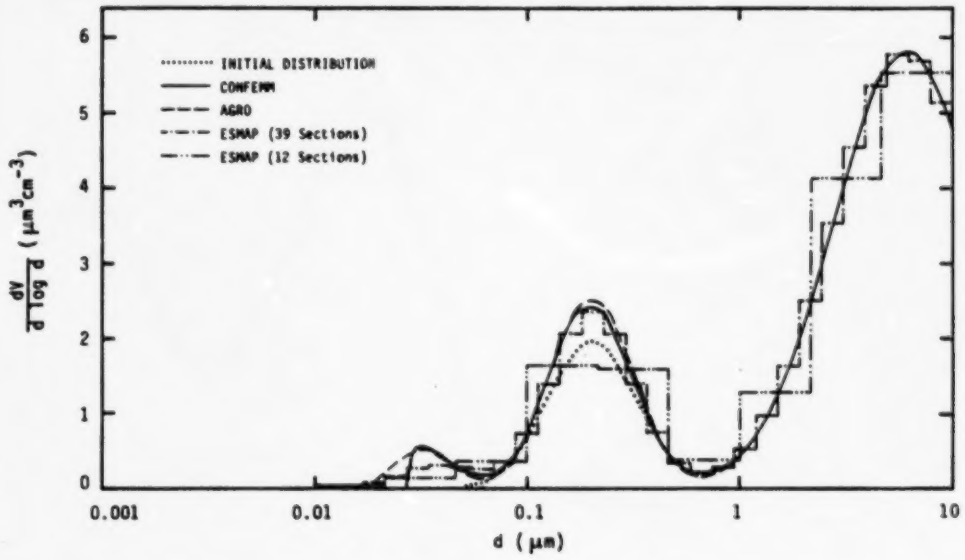
For the model simulations performed here, Gear's method of solving stiff ordinary differential equations was employed by COAGUL (Gear, 1971), and a modified version of Gear's method (Byrne and Hindmarsh, 1975) was used by ESMAP. In AGRO, the nonstiff ordinary differential equations were solved by a finite-difference method.

The computational times on a PRIME 750 computer were as follows. AGRO required less than 1 CPU s for the 12-hr simulation. COAGUL required from 100 to 1000 CPU s, depending on the case study. ESMAP required from 180 to 2500 CPU s with 39 sections and from 40 to 350 CPU s with 12 sections. For the initial ESMAP simulation, approximately 500 extra CPU s were required to calculate the sectional coefficients for the simulations with 39 sections and 70 extra CPU s for those with 12 sections. The coefficients were stored and used for subsequent simulations. These computational times are given to indicate the magnitude of the computational requirements; they may vary if different numerical techniques are used to integrate the model's differential equations. It should also be noted that, when the aerosol dynamics equations are solved along with other differential equations such as those for chemical kinetics (e.g., Seigneur, 1982), the incremental cost of the aerosol dynamics computation may be significantly less than the computational costs reported here.

Simulation of Condensation

The results of the simulations of condensation are presented for the volume size distribution in Figures 5–7 for clear, hazy, and urban conditions. The results of the model performance evaluation are listed in Table 3.

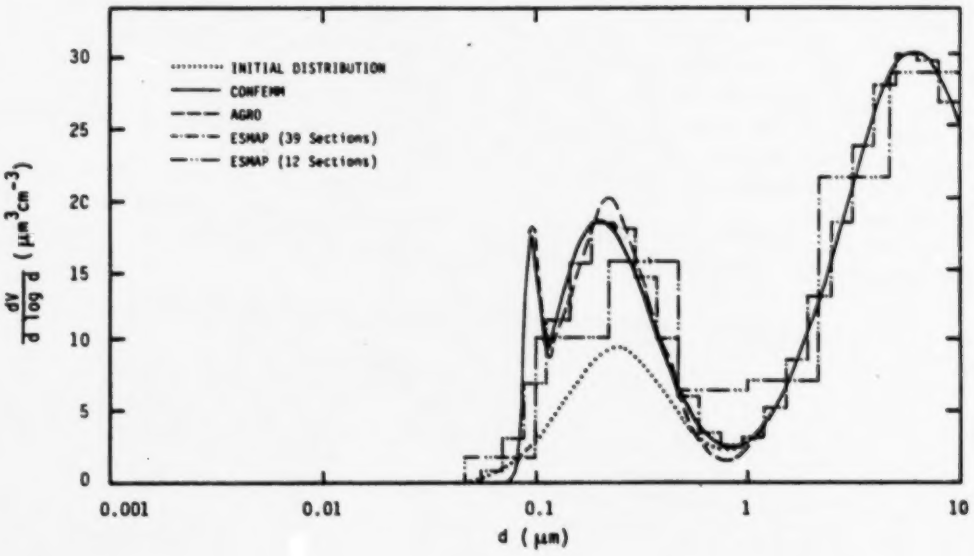
In theory, total aerosol number is conserved during condensation. The total aerosol number conservation was checked for



CONFEMM, ESMAP (both 12 and 39 sections), and AGRO. AGRO and ESMAP were found to conserve aerosol number to within at least 0.5% after 12 hr of simulation. CONFEMM was within 8.2%, 0.02%, and 3.7% for the clear, hazy, and urban cases. The larger error for CONFEMM occurs at

FIGURE 5. Simulation of condensation for clear conditions; aerosol volume distributions, initially and after 12 hr.

FIGURE 6. Simulation of condensation for hazy conditions; aerosol volume distributions, initially and after 12 hr.



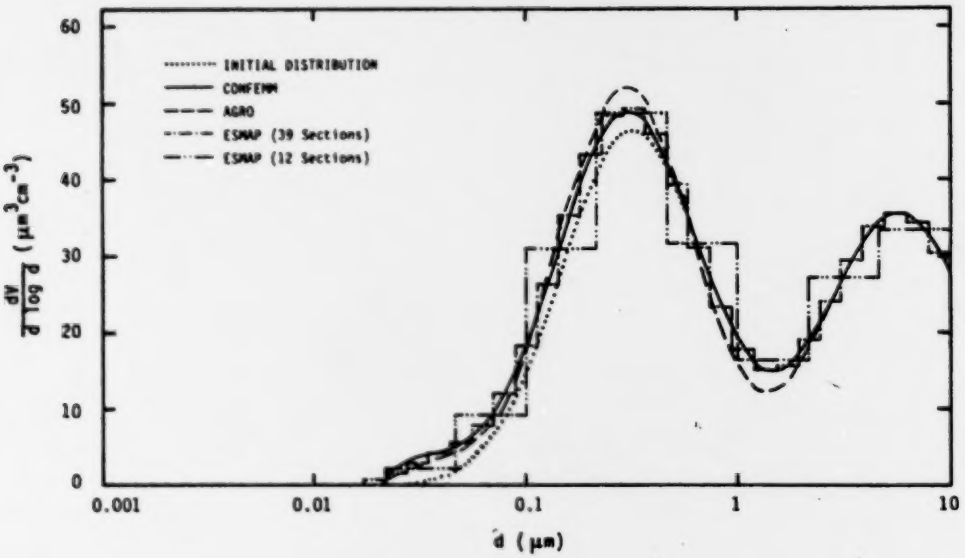


FIGURE 7. Simulation of condensation for urban conditions; aerosol volume distributions, initially and after 12 hr.

the lower range of the size distribution, where the very low mass concentrations and very high number concentrations induce errors in the calculation of the total number concentration by interpolation between grid points. This localized error in the total number concentration has very little effect on the accuracy over the entire size range, as demonstrated by the good agreement obtained between simulations performed with 40 and 80 grid points.

The CONFEMM simulation of condensation for clear conditions shows that secondary aerosols condense on two modes, with peak concentrations at about 0.03 and 0.2 μm. The mode centered at 0.03 μm results from the larger rate of condensation on smaller aerosols that is expressed by Eq. (4). The mode centered at 0.2 μm results from condensation that takes place at a slower rate but on a larger number of existing aerosols. It should be noted that if coagulation were simulated simultaneously, the lower mode would vanish owing to coagulation of these small aerosols with aerosols from the accumulation mode (Seigneur and Barnes, 1985).

ESMAP with 39 sections reproduces the existence of these two modes. However, because of numerical diffusion associated with

TABLE 3. Comparison of Model Simulation Results for Condensation

Model	Average absolute normalized difference (percent)		
	Clear conditions	Hazy conditions	Urban conditions
CONFEMM		(Reference)	
ESMAP (39 sections)	4	12	1
ESMAP (12 sections)	13	35	4
AGRO	6	18	7

the solution of the sectional condensation equation, the lower mode is more spread out in the ESMAP simulation. For aerosols with diameters above 0.07 μm, the ESMAP simulation results with 39 sections agree well with the CONFEMM simulation results. ESMAP with 12 sections underpredicts the formation of a mode below 0.1 μm. Too much numerical diffusion is associated with the size resolution used in ESMAP with 12 sections. Nevertheless, the ESMAP (12 sections) simulation results are within 13% of the CONFEMM simulation results, on average.

AGRO reproduces the two submicron modes. The lower mode is more spread out than in the CONFEMM simulation because of the log-normal distribution constraint of AGRO. Good agreement is obtained between the AGRO and CONFEMM simulation results above 0.03 μm.

The simulation of condensation for hazy conditions is a more difficult test of the condensation models because the volume of condensed aerosol amounts to about 50% of the initial fine aerosol volume. In the CONFEMM simulation, the lower mode is centered at about 0.1 μm and is more accentuated than it was in the clear-condition simulation. ESMAP fails to reproduce this lower mode because of numerical diffusion. AGRO reproduces the peak at 0.1 μm predicted by CONFEMM but predicts a slightly larger diameter for the accumulation mode peak. Because of numerical diffusion, ESMAP with 12 sections also predicts a larger median diameter for the accumulation mode. ESMAP with 39 sections performs better than ESMAP with 12 sections and AGRO and is able to reproduce the diameter of the peak of the accumulation mode predicted by CONFEMM. None of these models agrees within less than 10% with CONFEMM.

The simulation of condensation for urban conditions is not as difficult a test because the condensing volume relative to the initial fine aerosol volume is less, and the predominance of the accumulation mode over the nuclei mode precludes the formation of a distinct lower mode as shown in the CONFEMM simulation results. Therefore, this case is easier to simulate than were the previous cases. ESMAP performs very well with 39 sections and still offers very satisfactory performance with 12 sections. AGRO tends to overpredict the peak concentration of the accumulation mode because of the assumption of a log-normal size distribution. All models predict the same median diameter of the accumulation mode, which is nearly identical to that of the initial size distribution.

As was done in the ESMAP simulations of coagulation, the ESMAP simulations of condensation also employed the modified version of Gear's method to solve stiff ordinary differential equations (Byrne and Hindmarsh, 1975). AGRO used the same finite-difference technique used for coagulation. In CONFEMM, a finite-element method was used (Tsang and Brock, 1983).

The computational times on a PRIME 750 computer were as follows. AGRO required less than 1 CPU s for the 12-hr simulation. CONFEMM required about 150 CPU s. ESMAP with 12 sections required about 90 CPU s, and ESMAP with 39 sections required about 300 CPU s. Unlike the coagulation cases simulated with ESMAP, the extra CPU s required when the sectional coefficients were calculated for the first time were minimal, on the order of 10 s.

These CPU times are only approximate since, as mentioned in the previous section, they depend on the numerical technique of integration and could eventually be reduced by further optimizing the integration techniques.

CONCLUSION

A comparative review of mathematical models of aerosol coagulation and condensation has been presented. This review should provide useful guidance in selecting models according to computational requirements and the level of accuracy desired for a

particular application. Three approaches were presented that differ by their representation of the size distribution of aerosols and include continuous, sectional, and parametrized (log-normal) representations. The models COAGUL and CONFEMM were selected as representative of the continuous approach for simulating coagulation and condensation, respectively. These models appear to provide the most accurate solution to the aerosol dynamics equations and are thus used as references in this model comparison. The model ESMAP represents the sectional approach and was applied here with 39 sections (the finest size resolution allowed in its standard formulation) and 12 sections over the 0.001 to 10 μm aerosol diameter range. The model AGRO represents the parametrized approach; it is based on a trimodal log-normal representation of the aerosol size distribution.

COAGUL and CONFEMM require the solution of 40 differential equations; ESMAP, 39 and 12, depending on sectional resolution, and AGRO, 6. The computational times on a PRIME 750 computer for 12 hr of simulation of coagulation or condensation are less than 1 CPU s for the AGRO model and range from 90 to 3000 CPU s for the other models.

Simulations of coagulation and condensation were conducted for 12 hr with initial aerosol size distributions typical of clear, hazy, and urban atmospheric conditions. The results of these simulations may be summarized as follows.

For coagulation ESMAP with either 39 or 12 sections performs very well relative to COAGUL, i.e., the aerosol size distributions calculated by these models are within a few percent. AGRO performs well for clear and hazy conditions where coagulation has little effect on the initial size distribution but is less accurate (within 18% of COAGUL on average) for urban conditions. This poorer performance of AGRO is due to its inherent assumption of the log-normal distribution, which leads to overprediction of the coagulation rate.

For condensation, ESMAP requires a relatively large number of sections to minimize numerical diffusion. The performance of ESMAP with 39 sections is satisfactory for all cases, whereas with 12 sections it produces reasonable results when condensation occurs primarily on the accumulation mode but poorer results when condensation also occurs on smaller aerosols to form a mode below 0.1 μm in addition to the accumulation mode. AGRO tends to overestimate the peak concentration of the accumulation mode, but it predicts the median diameter of the mode fairly well.

These results suggest that, for the conditions considered, ESMAP accurately simulates aerosol dynamics, although the presence of numerical diffusion may require the use of a larger number of sections to simulate condensation accurately. AGRO performs satisfactorily but tends to overestimate coagulation rates and the peak concentration of the accumulation mode resulting from condensation. Its substantially lower computational time compared to that of the other models makes AGRO attractive for applications that have large calculational requirements; however, the model-accuracy limitations must be kept in mind.

Both AGRO and ESMAP can treat coagulation and condensation simultaneously. Because coagulation has a strong effect on the size distribution of an aerosol undergoing condensational growth (Seigneur and Barnes, 1985), it would be useful to compare these two models with one based on the models of the continuous representation of the aerosol size distribution that simulates simultaneous coagulation and condensation. Tsang and Brock (1985) recently developed such a model to solve the general dynamic equation for simultaneous coagulation, condensation, and evaporation processes with changing saturation ratio.

For application purposes, each one of these three methods has its merits, and the selection of a specific approach will depend on the requirements of the application. For example, if aerosol dynamics is incorporated

within a larger model describing fluid dynamics and ambient chemistry, a low computational cost may be required for the aerosol dynamics calculation to keep the overall computational cost within a reasonable range. This constraint may preclude use of a computationally expensive approach and favor the less expensive but less accurate approaches. On the other hand, the simulation of a laboratory experiment conducted to elucidate the details of a physical process of aerosol dynamics will require an accurate solution, and the accurate but computationally more expensive approaches may then be needed.

The results of this comparative study apply to atmospheric aerosols and depend on the test cases chosen. However, the conclusions of this work can be qualitatively extended to the simulation of particulate systems in general and should prove helpful for the selection of a mathematical model for studies of particulate dynamics.

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